PATENT SPECIFICATION

NO DRAWINGS

Inventor: ALAN BURGOYNE DAVIES

908,988

Date of filing Complete Specification Aug. 18, 1959

PATENTS ACT, 1949

SPECIFICATION NO. 908,988

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 18th day of June, 1963 this Specification has been amended under Section 29 in the following manner:-

Page 3, *after* line 107, *insert*

"The tests described were then applied to the treated paper, the results of the tests being shown in the table below."

Test or nature of Staining media	Untreated Wallpaper	Wallpaper treated as described in Example 1.
Spray Rating	0	100
Wet Rub Fastness Ink Staining Test	10 Heavy staining could not be removed without destroying the surface of the paper.	200+ Stain completely removed
Oil Spots, grease etc.	As above	Stain could be removed by wiping with a dry cloth followed by one damped with solvent.
Pencil and Crayon marks	As above	Easily removed with a solvent damped cloth
Greasy finger marks	As above	It was almost impossible to mark the treated paper, any stain could be removed with a solvent damped cloth.
Jams, sauces, coffee and tea stains	As above	All easily removed with a damp cloth.

Attention is also directed to the following printer's error:-

Page 1 in the heading, *for* "(Patent of Addition to No. 766,864 dated Nov. 24, 1955.)" *read* "(Patent of Addition to No. 766,864 dated March 24, 1955.)"

THE PATENT OFFICE,
14th August, 1963

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PATENT SPECIFICATION

NO DRAWINGS

Inventor: ALAN BURGOYNE DAVIES

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(Patent of Addition to No. 766,864 dated Nov. 24, 1955).

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Index at acceptance: —Classes 2(7), T6(D8:F1:F2:J1:J2C:J5:J6); 2(6), P4C(13A:14A:14B), P4D(1A:3B1), P10C(13A:14A:14B), P10D1A; and 140, E1(A:C).

International Classification: —C08g. C08f. D21h.

COMPLETE SPECIFICATION

Organosiloxane Compositions for the Treatment of Paper

We, MIDLAND SILICONES LIMITED, a British Company, of 68, Knightsbridge, London, S.W.1, formerly of 19, Upper Brook Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of paper and paper products to render them water-repellent and stain-resistant and is concerned with a modification of the invention of our Specification No. 766,864.

It is well known that organopolysiloxanes can be applied to paper and other organic materials to render them water-repellent and non-adherent to sticky surfaces. Our Specification No. 804,198 claims *inter alia* a siloxane-in-water emulsion for the treatment of paper, comprising a methyl-hydrogenpolysiloxane and a hydroxylated methyl siloxane. However, although these siloxanes impart a high degree of water-repellency to paper, the treated paper has a poor wet rub-fastness and resistance to staining by oils and greases.

It is also well known that organic film-forming resins, such as polyvinyl acetate and acrylic resins, can be used for the treatment of paper to impart to the surface of the paper a certain amount of stain resistance. The film formed by these resins however, has only a limited degree of water-repellency and is softened and finally removed on sponging with solvent.

Hitherto, the treatment of paper with the above mentioned compositions has not been entirely satisfactory for the reasons already given. For example, when wallpaper is treated with the mixture of siloxanes of our Specification No. 804,198 it is found that the removal of stains from the wallpaper by rubbing with a damp cloth results in the loss of the water-repellent and stain resistant characteristics of the paper. On the other hand the treatment of, for example, wallpaper with an organic film-forming resin alone results in a film on the surface of the paper which possesses a degree of water-repellency somewhat poorer than that given by the siloxanes and which film may be easily removed on rubbing with a solvent damped cloth.

We have now found that paper having superior wet-rub fast, water-repellent, stain-resistant and release properties may be obtained by the application to it of certain organopolysiloxanes in conjunction with a synthetic organic film-forming resin.

According to the present invention, a process is provided for treating paper and paper products wherein the paper or paper product is treated with a composition comprising:—

(1) (a) from 0.1 to less than 5% by weight of an alkylhydrogen polysiloxane, and (b) from 99.9 to more than 95% by weight of a polysiloxane of the general formula $R_xSiO_{\frac{4-x}{2}}$ where each R is an alkyl radical and x has a value of from 1.4 to 2.3 inclusive and which polysiloxane may or may not be hydroxylated, and (2) a synthetic organic film-forming resin.

The present invention also includes paper or a paper product having a film of a composition comprising:—

(1) (a) from 0.1 to less than 5% by weight of an alkylhydrogen polysiloxane, and (b) from 99.9 to more than 95% by weight of a polysiloxane of the general

[*Price* 4s. 6d.]

Price 75p

formula $R_xSiO_{\frac{4-x}{2}}$ where each R is an alkyl radical and x has a value of from 1.4 to 2.3 inclusive, and which polysiloxane may or may not be hydroxylated, and (2) a synthetic organic film-forming resin.

The term "alkylhydrogenpolysiloxane" as employed herein includes siloxanes of the general formula $R_xH_ySiO_{\frac{4-x-y}{2}}$ where R has the meaning given above and x=0.5 to 2.3 and y=1.5 to 0.2.

The polysiloxanes (b) may consist of recurring units of the type R_2SiO or co-polymers of R_2SiO, $R_3SiO_{0.5}$ and $RSiO_{1.5}$ units. Some or all the molecules of the polysiloxane (b) may contain at least two silicon-bonded hydroxyl groups attached thereto. Thus the polysiloxanes (b) which may be employed include hydroxylated diorganosiloxanes, hydroxylated co-polymers of diorganosiloxane and mono-organosiloxane and mixtures of these hydroxylated polysiloxanes with the non-hydroxylated organopolysiloxanes hereinbefore described, the organic substituents on the above organosiloxanes being alkyl groups.

Specific examples of synthetic organic film-forming resins which can be employed in the present invention are acrylic resins, vinyl acetate, polyvinyl alcohol, vinyl chloride, aminoplast and phenol-formaldehyde resins. These resins are all well known commercial products and as such can be obtained in a variety of forms. For example some are water-soluble and may be obtained in aqueous solution while others may be obtained as aqueous emulsions. Some of these synthetic organic film-forming resins have been found to be slightly more suitable for one application than others. For example polyvinyl alcohol is more suitable where the release properties of the paper are important than for example for the production of stain-resistant wallpaper.

When it is desired that the synthetic organic film-forming resin and the polysiloxane be applied simultaneously to the substrate from the same treating solution it will of course be necessary that the emulsion or solution of the synthetic organic film-forming resin be compatible with the emulsion or solution of the polysiloxane component. Such compatibility is however not essential when the substrate is treated by the two-bath process, that is, when the synthetic organic film-forming resin is applied prior to the application of the polysiloxane component. Polyvinyl acetate is especially suitable as a synthetic organic film-forming resin.

The compositions used in this invention may be applied either in solvent solution or in emulsion form. With the higher molecular weight siloxanes it is sometimes preferable to use a solution, although this is not essential since the solution of the higher molecular weight siloxanes can be emulsified if desired.

The synthetic organic film-forming resin may be applied before or simultaneously with the siloxane, but we have found that, in general, the paper of this invention is most conveniently prepared by applying thereto a mixture of emulsions of the polysiloxane and synthetic organic film-forming resin, or when the synthetic organic film-forming resin is water-soluble, by applying to the paper a mixture of a polysiloxane emulsion and an aqueous solution of the synthetic organic film-forming resin.

Although the relative amounts of siloxane and synthetic organic film-forming resin in the compositions of this invention are not critical and can vary over a wide range it has been found preferable to employ a mixture which contains between 7 and 25 parts by weight of siloxane for every 100 parts of organic resin. Less than 7 parts of the siloxane leads to poor water-repellency and more than 25 parts is uneconomical and does not necessarily give a better product. However, a further feature of this invention is the excellent release properties imparted to paper when treated with the compositions used in the present invention, highly satisfactory release of bitumen being obtained from paper to which has been applied an emulsion containing as little as 4 parts of siloxane for every 100 parts of organic resin.

The method of application of the compositions used in this invention to the paper will depend to some extent on whether it is desired to treat one or both surfaces of the paper. For most applications the paper is best treated either by roller coating, brush coating, knife coating or spraying.

After the paper has been treated with the siloxane-synthetic organic film-forming resin mixture it is heated to dry it and cure the siloxane, 2 to 5 minutes at 100—120° C. usually being sufficient to dry the coating and render it water-repellent and stain-resistant. Although desirable in most cases this heat treatment is not essential, as the paper may be treated and its coating allowed to dry and cure at room temperature.

In order to hasten the cure it may be desirable to employ a setting catalyst for the siloxane. The preferred catalysts for this purpose are well known in the art, for example, the metal salts of carboxylic acids such as lead, octoate, dibutyltin dilaurate, stannous octoate, zinc octoate and zinc naphthenate.

By dilution of the treating solution or

emulsion the build up of the water-repellent and stain-resistant film on the paper can be controlled. However, the thickness of this film is also dependent upon the type of paper being treated and the method employed for applying the protective film. Thus, although the appropriate dilution of the treating composition will depend upon individual circumstances, we have found that paper having excellent properties is obtained if conditions are adjusted such that the treated paper has deposited thereon a film which is from 0.0005 to about 0.001 inches thick.

The compositions used in the present invention can be used to treat papers such as wallpapers, decorative paper, Kraft paper, Bond paper, cartridge paper, cover papers, map paper, paper board and chip board.

Paper and paper board treated in accordance with this invention show excellent release and stain-resistant properties to such materials as bitumen, oils, greases, milk, tea and coffee, and can be used in the fabrication of bags, containers, maps, table mats and the like where such properties are advantageous.

Our co-pending Application No. 16870/58 (Serial No. 852,596) claims a composition suitable for rendering paper and paper products non-adherent comprising an emulsion or solution containing (1) a mixture of (a) from 0.1% to less than 5% by weight of a methylhydrogensiloxane, trimethylsiloxy end-blocked methylhydrogensiloxane or a mixture thereof and (b) 95 to 99.9% by weight of a hydroxylated methylpolysiloxane of the general formula $Me_xSiO_{\frac{4-x}{2}}$ where Me is a methyl radical and x has a value of from 1.9 to 2.0 inclusive having a viscosity of at least 100 cs. at 25° C., and having at least two silicon-bonded hydroxyl groups in substantially all the molecules, (2) an aminoplast resin or a phenol-aldehyde resin in such an amount that the weight ratio of siloxane mixture (1) to resin (2) is from 1:10 to 10:1, and (3) a siloxane curing catalyst. The said specification also claims paper rendered non-adherent with a coating obtained by curing the said composition. We make no claim herein to anything claimed in our co-pending Application No. 16870/58 (Serial No. 852,596).

The following examples illustrate the invention.

EXAMPLE 1

The siloxane employed had a composition of 97% by weight of a liquid hydroxylated dimethylpolysiloxane having a viscosity of 300 cs. at 25° C. and 3% by weight of a trimethyl end-blocked methylhydrogenpolysiloxane having a viscosity of 40 cs. at 25° C.

This siloxane mixture was emulsified in water to give 40% by weight of total silicone solids calculated on the weight of the emulsion.

An emulsion of zinc octoate and dibutyl tin diacetate was added to this in an amount sufficient to give 2% by weight of zinc and 0.34% by weight of tin calculated on the weight of total silicone in the emulsion. The silicone-catalyst mixture was then added to a bath containing an aqueous emulsion of a polyvinyl acetate resin so that the bath contained 18 parts of siloxane for every 100 parts of resin.

The emulsion was then applied to wallpaper, the treated paper allowed to dry and then heated for 2 minutes at 120° C.

The treated papers were tested together with untreated papers by the following test methods:—

1. SPRAY RATING.
2. WET RUB FASTNESS—the paper being rubbed hard with a damp cloth, the number of times the cloth passed over the paper before a change in the surface of the paper was noticed, was recorded.
3. INK STAINING TEST—a blot of "Stephens" Permanent Red Ink, which is only partially soluble in water was deposited on the paper and allowed to stand for one minute.

The surplus ink was removed with a piece of blotting paper, the stain being then (a) sponged with a clean cloth soaked in detergent solution, (b) dried, (c) finally removed with a solvent damped cloth.

In addition, the ease of removal of the following household stains was recorded.

1. Oil and grease spots.
2. Stains left by jams, sauces, coffee and tea.
3. Pencil and crayon marks.
4. Greasy finger marks.

EXAMPLE 2

Twelve parts of the catalysed siloxane emulsion of Example 1 were added to a treating bath containing an emulsion comprising 4 parts of polyvinyl alcohol, 35 parts of polyvinyl acetate and 49 parts of water.

Kraft paper was then treated with the mixture and after being allowed to dry for a short period was heated for two minutes at 120° C.

The paper was then used to make up small packets with the coated surface inside. Hot bitumen was then poured into several of the packets and allowed to cool. It was found that the paper packets could be easily stripped from the solidified contents.

Similar results were obtained when paraffin wax was substituted for bitumen.

Subject to the foregoing disclaimer, what we claim is:—

1. A process for treating paper and paper products wherein the paper or paper product is treated with a composition which comprises:—

(1) (a) from 0.1 to less than 5% by weight of an alkylhydrogen polysiloxane, and (b) from 99.9 to more than 95% by weight of a polysiloxane of the general formula $R_xSiO_{\frac{4-x}{2}}$ where each R is an alkyl radical and x has a value of from 1.4 to 2.3 inclusive, and which polysiloxane may or may not be hydroxylated, and (2) a synthetic organic film-forming resin.

2. A process as claimed in Claim 1 wherein the organic film-forming resin is polyvinyl acetate.

3. A process as claimed in Claim 1 or 2 wherein the alkylhydrogen polysiloxane is a methylhydrogen polysiloxane.

4. A process for treating paper and paper products substantially as described with reference to Example 1.

5. A process for treating paper and paper products substantially as described with reference to Example 2.

6. Paper or a paper product which has a film of a composition comprising:—

(1) (a) from 0.1 to less than 5% by weight of an alkylhydrogen polysiloxane, and (b) from 99.9 to more than 95% by weight of a polysiloxane of the general formula $R_xSiO_{\frac{4-x}{2}}$ where each R is an alkyl radical and x has a value of from 1.4 to 2.3 inclusive, and which polysiloxane may or may not be hydroxylated, and (2) a synthetic organic film-forming resin.

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